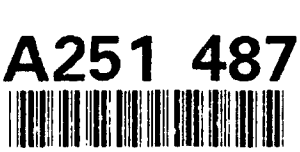

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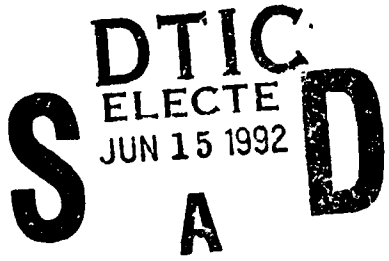
Final Report

Fabrication and Galvanic Protection of Carbon Zirconia Composites

ONR research contract no. N00014-88-K-0519

1991



Gerald P. Wirtz

Department of Materials Science and Engineering
University of Illinois at Urbana-Champaign

Overview of the Program

Carbon and graphite are well known to have outstanding structural properties at very high temperatures. The principal limitation on their use is the oxidation of the carbon to form the gaseous oxides of carbon in oxidizing environments. This project was a three year program, funded for a total of $300,000, to investigate the feasibility of coating porous carbon or graphite substrates with yttria stabilized zirconia (YSZ) by electrochemical vapor deposition (EVD), and using the electrolytic properties of the coating to cathodically protect the carbon from oxidation at high temperatures. With the application of an electric field, the resulting composite should withstand oxidation at temperatures well above those possible by protection by simple physical barrier coatings.

The program was divided into two parts, the study of the oxidation reaction at the interface between the carbon and the solid electrolyte, and the study of the deposition of yttria stabilized zirconia on a carbon substrate. The former was studied by making permeation studies using a Bunsen tower to measure the volume of CO gas produced by the oxidation of the carbon electrode on the electochemical cell. The deposition was studied in a reaction chamber where the metal chloride vapors were obtained by sublimation of the solid chlorides. The composition was varied by varying the temperature of the sublimation sources independently. Carbon monoxide was used as the oxidizing agent throughout.

Significant Results

At no time did it appear that the oxidation rate of the carbon electrode was controlled by the rate of oxygen permeation through the electrolyte barrier. The rate limiting step under zero field conditions was always either the interfacial oxidation reaction or the gas phase diffusion of reaction products away from the reaction site.

The thermodynamic feasibility of depositing yttria stabilized zirconia from the metal chlorides using CO as the oxidizing medium was demonstrated both experimentally and by thermodynamic calculation. The initial experimental demonstration was accomplished by depositing YSZ on an impervious tube of YSZ, to eliminate the vagaries associated with the porosity and reactivity of a carbon substrate. At the oxygen partial pressures represented by the chloride vapors on one side and CO on the other, the YSZ substrate exhibited sufficient electronic conductivity to permit rapid growth on a thick non-porous substrate. Coatings deposited on YSZ substrates were always cubic, sometimes with the characteristic {220} texture, and usually with a lattice constant different from the substrate. Two recognizably different lattice constants could often be associated with the coating itself.

Subsequent films were grown on porous graphite substrates of 18, 28 and 48% porosity. Normally, the films deposited on porous graphite showed a porous morphology deep in the graphite pores, becoming more dense as it approached the surface, and spreading across the surface as a completely dense coating with small, equiaxed, well faceted grains. Both cubic YSZ, as well as partially stabilized tetragonal zirconia were produced, depending on the growth conditions. Importantly, the tetragonal PSZ was more adherent and less susceptible to spalling due to the thermal expansion mismatch between substrate and coating. The adherence was also strongly influenced by the rate of cooling of the composite from the deposition temperature. It is tentatively proposed that by preferred orientation of the c-axis of some grains along the equivalent cube axis closest to the surface of the interface during cooling, the difference in thermal expansion can be accomodated in the tetragonal phase.

List of Publications

G. P. Wirtz, Y. Huang and H. D. DeFord, "Electrode Processes for Carbon in Contact with Yttria Stabilized Zirconia" Ceramic. Trans., 24, 397-406 (1991)

G. P. Wirtz, "Electrochemical Vapor Deposition of Oxide Films", Morris E. Fine Symposium, Pp 221-230, ed., P. K. Liaw, J. R. Weertman, H. L. Marcus and J. S. Santer, The Mineral Metals and Materials Society, Warrendale PA (1991)

Two other manuscripts are in preparation and a third is tentatively planned.

Students Receiving Degrees from this Project

Yutung Huang, M.S. in Ceramic Engineering, 1991

Lih-Farn Shiau, Ph.D. in Materials Science and Engineering, expected 1993

H. Dale DeFord, Ph.D. in Ceramic Engineering, expected 1993

Work on this project will continue through May of 1993 with the support of the Research Board of the University of Illinois.

Summary

It has been demonstrated that it is feasible to form a dense, pore-free coating of yttria stabilized zirconia on a porous graphite substrate by electrochemical vapor deposition. It appears that under appropriate conditions the structural integrity of the composite may be retained during slow heating and cooling, in spite of the gross mismatch in the thermal expansion coefficients of the coating and substrate. It is hypothesized that the thermal expansion difference is accomodated in the tetragonal zirconia phase by the preferential alignment of the c-axis along the pinacoidal direction closest to the interfacial plane via a displacive transformation during cooling.